

PCT/GB 00/02363



INVESTOR IN PEOPLE



PRIORITY DOCUMENT

SUBMITTED OR TRANSMITTED IN
COMPLIANCE WITH RULE 17.1(a) OR (b)

The Patent Office
Concept House
Cardiff Road
Newport
South Wales
NP10 8QQ

REC'D 17 AUG 2000

WIPO

PC

GB 00/02363

I, the undersigned, being an officer duly authorised in accordance with Section 74(1) and (4) of the Deregulation & Contracting Out Act 1994, to sign and issue certificates on behalf of the Comptroller-General, hereby certify that annexed hereto is a true copy of the documents as originally filed in connection with the patent application identified therein.

In accordance with the Patents (Companies Re-registration) Rules 1982, if a company named in this certificate and any accompanying documents has re-registered under the Companies Act 1980 with the same name as that with which it was registered immediately before re-registration save for the substitution as, or inclusion as, the last part of the name of the words "public limited company" or their equivalents in Welsh, references to the name of the company in this certificate and any accompanying documents shall be treated as references to the name with which it is so re-registered.

In accordance with the rules, the words "public limited company" may be replaced by p.l.c., plc, P.L.C. or PLC.

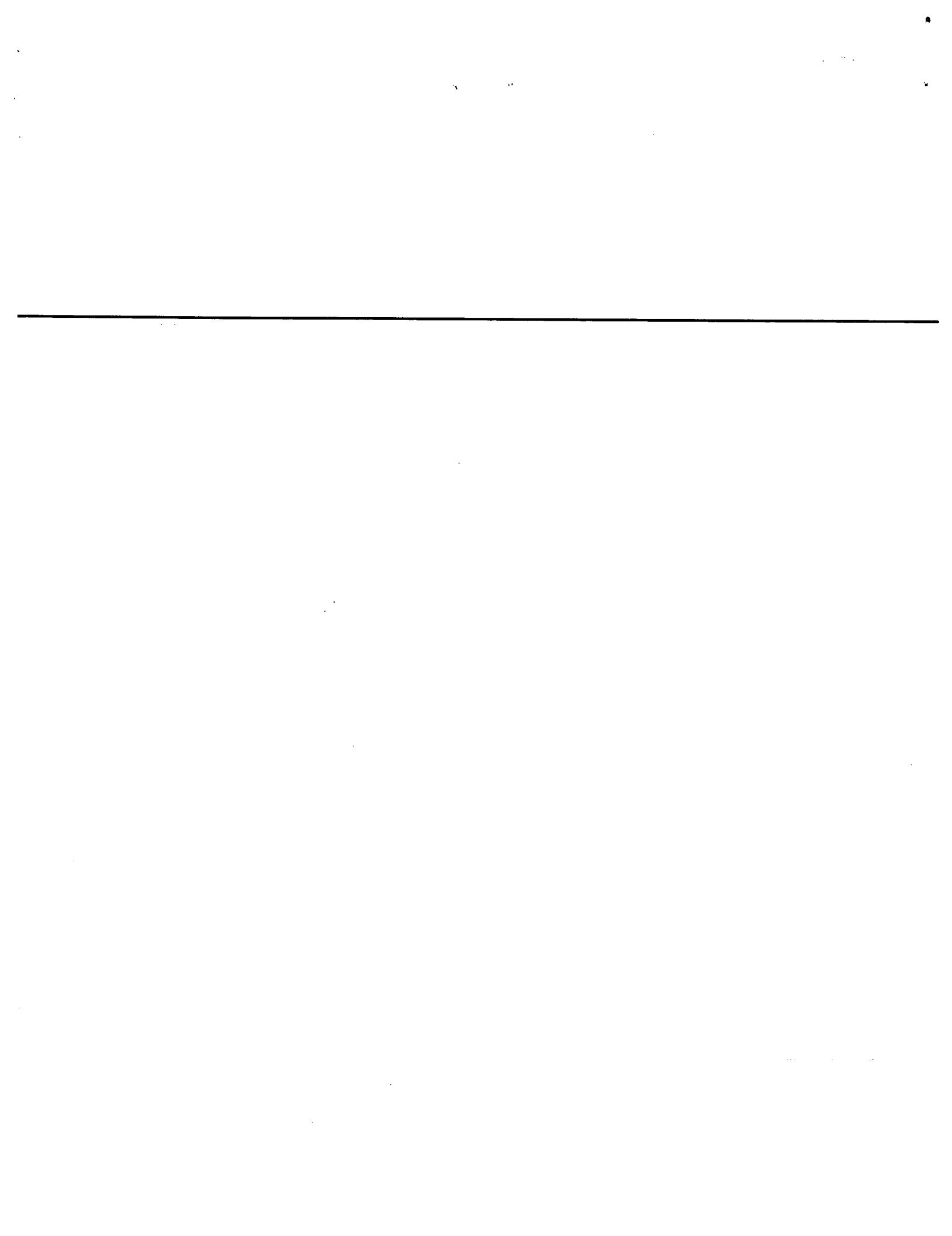
Re-registration under the Companies Act does not constitute a new legal entity but merely subjects the company to certain additional company law rules.

Signed

Andrew Garsley

Dated

18 July 2000



For your use

THE PATENT OFFICE
A
- 7 JUL 1999
RECEIVED BY FAX

07JUL99 E460253-1 D02635
P01/7700 0.00 - 9915857.8

Your reference
GS/AMW/P61575A

Notes

Please type, or write in dark ink using CAPITAL letters. A prescribed fee is payable for a request for grant of a patent. For details, please contact the Patent Office (telephone 071-438 4700).

16 of the Patents Rules 1990 is the main rule governing the completion and filing of this form.

2 Do not give trading styles, for example, 'Trading as XYZ company', nationality or former names, for example, 'formerly (known as) ABC Ltd' as these are not required.

Warning

After an application for a Patent has been filed, the Comptroller of the Patent Office will consider whether publication or communication of the invention should be prohibited or restricted under Section 22 of the Patents Act 1977 and will inform the applicant if such prohibition or restriction is necessary. Applicants resident in the United Kingdom are also reminded that under Section 23, applications may not be filed abroad without written permission unless an application has been filed not less than 6 weeks previously in the United Kingdom for a patent for the same invention and either no direction prohibiting publication or communication has been given, or any such direction revoked.

**The
Patent
Office**

Request for grant of a Patent 9915857.8

Form 1/77

Patents Act 1977

1 Title of invention

METHOD

- 1 Please give the title of the invention

2 Applicant's details

- First or only applicant

- 2a If you are applying as a corporate body please give:

Corporate name
UNIVERSITY OF LEEDS

Country (and State of incorporation, if appropriate)

UNITED KINGDOM

- 2b If you are applying as an individual or one of a partnership please give in full:

Surname

Forenames

- 2c In all cases, please give the following details:

Address

LEEDS
WEST YORKSHIRE

UK postcode LS2 9JT
(if applicable)

Country UNITED KINGDOM

ADP number
(if known)

79832202

*2d, 2e and 2f:
If there are further applicants
please provide details on a separate
sheet of paper.*

Second applicant (if any)
2d If you are applying as a corporate body please give:
Corporate name

Country (and State of incorporation, if appropriate)

2e If you are applying as an individual or one of a partnership please give in full:

Surname

Forenames

2f In all cases, please give the following details:

Address

UK postcode
(if applicable)

Country

ADP number
(if known)

3
An address for service in the United Kingdom must be supplied.

Please mark correct box

Yes No → go to 3b

Please give details below
Agent's name

URQUHART-DYKES & LORD

Agent's address

TOWER HOUSE

MERRION WAY

LEEDS

Postcode LS2 8PA

Agent's ADP 1644004

'b:
*I you have appointed an agent,
all correspondence concerning
our application will be sent to
the agent's United Kingdom
address.*

3b If you have not appointed an agent please give a name and address in the United Kingdom to which all correspondence will be sent:

Name

Address

Postcode
ADP number
(if known)

Daytime telephone 1132452388
number (if available)

4 Reference number

4 Agent's or applicant's reference number
(if applicable) GS/AMW/P61575A

5 Claiming an earlier application date

5 Are you claiming that this application be treated as having been filed on the date of filing of an earlier application?

Please mark correct box Yes No go to 6

Please give details below

Please mark correct box

number of earlier application or patent number

filing date *(day month year)*

and the Section of the Patents Act 1977 under which you are claiming:

15(4) (Divisional) 8(3) 12(6) 37(4)

Please mark correct box

6 Declaration of priority

6 If you are declaring priority from a previous application(s), please give:

Country of filing	Priority application number <i>(if known)</i>	Filing date <i>(day,month,year)</i>
UNITED KINGDOM	9915346.2	01/07/1999

6

If you are declaring priority from a PCT Application please enter 'PCT' as the country and enter the country code (for example, GB) as part of the application number.

Please give the date in all number format, for example, 31/05/90 for 31 May 1990.

7

- The answer must be 'No' if:
- any applicant is not an inventor
 - there is an inventor who is not an applicant, or
 - any applicant is a corporate body.

8

Please supply duplicates of claim(s), abstract, description and drawing(s).

Please mark correct box(es)

9

You or your appointed agent (see Rule 90 of the Patents Rules 1990) must sign this request.

Please sign here

A completed fee sheet should preferably accompany the fee.

7 Inventorship

- 7 Are you (the applicant or applicants) the sole inventor or the joint inventors?

Please mark the correct box

Yes No

A statement of Inventorship on Patents Form 7/77 will need to be filed (see Rule 15).

8 Checklist

- 8a Please fill in the number of sheets for each of the following types of document contained in this application.

Continuation sheets for this Patents Form 1/77

Claim(s)

Description 16

Abstract

Drawing(s) 6

- 8b Which of the following documents also accompanies the application?

Priority documents (please state how many)

Translation(s) of Priority documents (please state how many)

Patents Form 7/77 - Statement of Inventorship and Right to Grant (please state how many)

Patents Form 9/77 - Preliminary Examination/Search

Patents Form 10/77 - Request for Substantive Examination

9 Request

I/We request the grant of a patent on the basis of this application.

Signed

Date 07/07/1999

(day month year)

Please return the completed form, attachments and duplicates where requested, together with the prescribed fee to:

The Comptroller
The Patent Office
Cardiff Road
NEWPORT
Gwent
NP9 1RH

The Comptroller
The Patent Office
25 Southampton Buildings
London
WC2A 1AY

-1-

METHOD

The present invention relates to a method for producing highly oriented mesophase pitch-based tapes and for producing highly oriented bulk carbon materials from the highly oriented mesophase pitch-based tapes, and to the tapes and the bulk carbon materials per se.

~~The graphite crystal is rendered highly anisotropic by its~~ structure which is composed of stacks of multiple sheet-like layers of carbon atoms (graphene layers). In the plane of the sheets, the carbon atoms are covalently bonded by sp^2 hybridisation of the electron orbitals. These layer planes are weakly held together by Van Der Waals forces. The graphite has exceptionally high stiffness (1060GPa) and strength (106GPa) and extremely high thermal conductivity within the basal plane (seven times higher than that of most conductive metals such as copper and silver, about thirty times higher in specific terms). It follows that in an article made of perfectly aligned graphene planes, the material would have extremely high strength in the basal plane directions since the load would be opposed by the covalent bonds themselves.

There are no artificial bulk carbon and graphite materials available with properties as good as the graphite crystal. However, there are carbon and graphite materials which have realised a fraction of these properties. An extremely wide range of properties may be engineered in carbon materials which may be produced from a variety of precursors through different processing routes. Carbon materials are widely used and play an essential role in aerospace, nuclear, metallurgical, chemical, mechanical and electrical applications.

-2-

Polygranular carbon and graphite are the main carbon materials from which engineering materials are made. Bulk materials (such as electrodes used for steel making and anodes for the aluminium industry) are produced from carbonaceous filler particles (cokes, graphite or carbon black) combined with a pitch binder. The raw materials are mixed to ensure even distribution of the binder and then ~~formed by extrusion or moulding. The bulk product is calcined~~ and the pitch binder decomposes to carbon. A high temperature of $>2500^{\circ}\text{C}$ is required to convert the carbon to graphite. At this stage the graphite density is the order of 1.7 Mgm^{-3} with a porosity in the region of ~25%. Thus the fabrication process usually requires lengthy, multiple pitch impregnation and pyrolysis cycles to reduce the porosity.

The properties of the filler coke particles and pitch binder as well as the processing conditions strongly influence the properties of the final bulk graphite artefacts. Coke particles may show preferred orientation along the extrusion direction which is particularly true if anisotropic or "needle" cokes are used giving an electrode with anisotropic properties. The properties of carbon and graphite materials produced in this way are complicated by the anisotropic nature of the crystallites but (generally speaking) they are porous, of low strength and have low transport properties. The bulk anisotropic properties are dependent on the size and arrangement of crystallites within the structure.

The cokes used in this process are produced from petroleum pitches. During pyrolysis most pitches pass through a discotic nematic liquid crystal phase when the polyaromatic molecules align in domains. This is an essential stage in the formation of graphitising carbon from an organic precursor. It is known as the carbonaceous mesophase and has been

-3-

exploited to produce advanced carbon and graphite fibres and composites.

Mesophase may be formed in complex polycyclic aromatic hydrocarbon mixtures such as petroleum or coal tar pitches when heated within the temperature range 350-500°C [Brooks et al (1965). Carbon 3, p 185]. In the early stages of the transformation, mesophase precipitates from the pyrolysing matrix as small spheres. Within the central region the mesophase layers lie parallel to define the polar diameter but curve to meet the interface with the pitch matrix at a high angle. As pyrolysis proceeds, these mesophase spheres grow and coalesce to larger spheres. Coalesced mesophase spheres show more complicated extinction patterns than the spheres which first appear (see Figure 1). As pyrolysis continues, the coalescence proceeds and eventually the material becomes entirely mesophase.

Certain mesophase pitches can be formed into fibres through melt spinning. The mesophase pitch melt is extruded through a multiple-hole spinneret. Under the combined effect of gravity and pulling of the roller, the extrudates are drawn down as they cool and eventually solidify to form the fibres. When molten mesophase pitch is forced through the spinneret, the planar polyaromatic molecules are lined up in the flow direction. The alignment is further improved during the fibre drawdown. Hence, the polyaromatic molecules are aligned more or less parallel to the fibre axis in the "as-spun" fibres thereby reducing the energy input required for graphitisation and producing fibres with exceptional stiffness. The spinning conditions have a strong impact on the degree of preferred orientation of "as-spun" fibres which is higher when the spinning viscosity is low at a high spinning temperature. It has been suggested that a pitch fibre with larger diameter and lower viscosity during

-4-

spinning provides a higher degree of preferred orientation because a pitch fibre with a thinner diameter cools more rapidly during the elongation process thereby inheriting a lower degree of preferred orientation as disordered states at higher temperature are locked in. The molecular structure of mesophase pitch also influences the shape, texture and degree of preferred orientation in the transverse direction.

In order to retain the fibre shape and the preferred orientation of mesophase molecules induced during spinning, "as-spun" fibres must be stabilised to render them infusible before further heat treatment. Stabilisation is normally achieved through oxidation in which the "as-spun" fibres are heated in an oxygen-containing atmosphere to temperatures between 200 and 350°C for a period of time sufficient to prevent fibres deforming and/or sticking during carbonisation. The stabilisation step can have a significant impact on the microstructure as well as the mechanical strength of the finished fibres. The oxygen absorbed by the fibre forms cross-linked aromatic structures that preserve the axial preferred orientation of the fibre during carbonisation and reduce the solubility of the fibre constituents. Two kinds of chemical reactions take place simultaneously during stabilisation. The first is oxygen uptake into the fibre constituents and the second is the evolution of volatile organic vapours and oxygen-containing gases. The weight gain is rapid in the early stages of oxidation but decreases with prolonged exposure. The amount of oxygen uptake is critical. It must be adequate to preclude interfusion of fibres yet low enough not to disrupt the fibre structure when it is eventually expelled as CO and CO₂ during carbonisation. An oxygen uptake of 6 to 7 wt% is known to be adequate for stabilisation.

-5-

Stabilised pitch fibres are infusible but they have poor mechanical properties, are fragile and difficult to handle. Thus carbonisation of the stabilised fibres is required to remove the remaining heteroatoms, improve mechanical properties and for mesophase pitch-based fibres to develop the layer structure. Graphitisation at temperatures up to 3000°C is a further option and is known to confer exceptional properties. Carbonisation involves elimination of non-carbon atoms which is completed at approximately 1500°C.

Graphitisation involves the development of graphitic order in the fibres. It sets in at temperatures above about 2000°C provided that the precursor is a graphitising one like mesophase pitch. It must be stressed that the two processes are continuous and that there is no distinct boundary between them. The temperatures quoted above are only intended as a rough guide to the completion and commencement of the two processes. The carbon fibres produced largely maintain the highly oriented structure of the "as-spun" fibres provided that they have been sufficiently well oxidised prior to carbonisation. Increasing the final heat treatment temperature brings about an increase in crystallite size and perfection and in the degree of preferred orientation of layer planes along the fibre axis thereby resulting in an improvement in mechanical and other properties.

The mechanical properties of pitch-based carbon fibres produced by Amoco are listed in Table 1 [Gerald et al (1991) Carbon 29, p 139]. These mesophase pitch-based carbon fibres have a high modulus which is very close to the theoretical value of single crystalline graphite.

-6-

Table 1. Properties of some pitch-based carbon fibres

Fibres	Diameter range μm	Tensile strength GPa	Young's modulus GPa	Elongation to failure %	Density Mg m^{-3}
Amoco P120s	9 - 15	2.2	827	0.3	2.18
Amoco P130x	9 - 14	2.87	923	0.3	2.19

Carbon fibres may have excellent mechanical and transport properties but only in one dimension. For effective use in composites they are combined in woven structures to give two, three and multi-dimensional properties. The formation of complete woven structures is an additional cost in the production of high performance composites.

The need for materials capable of withstanding the tremendous thermal erosion and thermal shock experienced by spacecraft and rockets has led directly to the development of carbon-carbon composites. A carbon-carbon composite is a carbon fibre-reinforced carbon matrix material. Carbon fibres are produced from a variety of precursors including pitch, polyacrylonitrile (PAN), vapour grown and rayon. The carbon matrix phase is typically formed by solid, liquid, or gaseous pyrolysis of an organic precursor material. Carbon-carbon composites seek to combine the high strength, stiffness and toughness of carbon fibre with the excellent thermomechanical properties of bulk polygranular carbons. There are two methods of formation of the carbon matrix, namely (1) chemical vapour deposition from a hydrocarbon gas (CVD) or (2) carbonisation of a carbonaceous resin or pitch.

The variety of structures displayed by carbon fibres and carbon matrices give the composite a broad range of properties (mechanical and physical). In addition, the interaction between the carbon fibres and the matrix carbons

-7-

plays an important role in determining the properties of the composite. Properties of carbon-carbon composites that make them attractive substitutes for other structural materials (such as metals and alloys) include high specific strength and stiffness, high temperature strength, high corrosion resistance, low thermal expansion, good friction and wear properties and high thermal and electrical conductivity. The use of these high performance materials has been developed in areas as diverse as integrated rocket throat nozzles, nosecones, aircraft brakes, structural materials in the aerospace industry, molten glass handling, golf clubs and biomedical implants.

The very high thermal conductivity of mesophase pitch-based carbon fibres is due to a highly oriented graphite crystalline structure along the fibre axis. The thermal conductivity of the mesophase pitch-based carbon fibre Thornel K-1100X is $1170 \text{Wm}^{-1}\text{K}^{-1}$ which is three times that of copper or 12 times in specific terms. One high profile application of mesophase pitch-based carbon fibre reinforced composites is their use as thermal management materials such as satellite radiators and electronic modules. Mesophase pitch-based carbon fibres are expensive and if processed into composites using the predominant CVI matrix infiltration route (which is extremely expensive) the cost of the products will be prohibitively high. Perceived new widespread applications such as heat sinks leads to a need for much more cost effective production methods.

As mentioned hereinbefore, the low mechanical and poor transport properties of polygranular materials are attributable to the high porosity and almost random orientation of the crystallites. An approach that reduces porosity is the method of producing so-called "sintered"

-8-

carbons, although the random orientation of crystallites still pervades.

Sintered carbons can be made by grinding a mesophase pitch into particles smaller than 10 μm , subjecting the particles to an oxidation treatment, forming the ground oxidised particles into desired shape and finally heating the shaped article to carbonise it. This ground mesophase has to be stabilised to a certain degree to control its thermoplasticity; too little thermoplasticity and the powder becomes undeformable and yields low green densities, too much thermoplasticity and the powder becomes too fluid and 'bloats'. The sintering of these powders differs significantly from the sintering of normal oxide ceramics. The intrinsic density of the powder increases progressively with heat treatment through to graphitisation temperatures. The powder shrinkage is due to the decrease in its inter-basal plane spacing (d_{002}) which approaches that of graphite crystal. Thus to produce high-density, high strength carbons the shrinkage of the bulk material must be matched by the shrinkage of the particles to avoid the formation of pores. Since the fine particles are directly bonded, high strength high-density bulk materials can be produced, although they have isotropic properties due to lack of preferred orientation of the crystallites.

Similar to the production of sintered carbon, highly oriented bulk carbon materials can be produced by pressing mesophase pitch-based fibres. This has been adopted in the so-called self-reinforcing method by pressing the as-spun mesophase pitch fibres into panels before thermosetting and further heat treatment [Barr et al, 22th Biennial Conf. on Carbon, 1995, p.32]. Amoco Performance Products Inc. recently developed a family of self-reinforced panels (ThermalGraph^R) from as-spun mesophase pitch fibres (average diameter ~10 μm). The high thermal conductivity of mesophase pitch-based carbon

-9-

fibres is attributable to the extended graphitic crystalline structure oriented along the fibre axis. However the extension of the graphitic layer structures normal to fibre axis is constrained by the geometric size of fibres. Moreover, the bulk density attainable can not be very high or the size of the bulk material is restricted due to the limit of the diffusion controlled stabilisation process. Interfibre porosities are evident from the microphotograph of ThermalGraph®. A further disadvantage is that the high thermal conductivity can only be achieved in one direction due to the one-dimensional orientation of the graphite crystals. Two-dimensional properties are difficult to achieve by simply aligning the fibres in two directions because of the circular geometry of the fibres.

Mesophase pitch-based carbon fibres may have different transverse textures which are prominent under a scanning electron microscope. Schematic drawings of the transverse textures commonly found in circular mesophase pitch-based carbon fibres are shown in Figure 2. The radial structure is the most commonly found transverse texture. It is believed that the transverse texture is "set in" during the extrusion of mesophase pitch through the spinneret and is preserved by stabilisation. There have been many attempts to produce noncircular fibres such as C-shaped, trilobal and rectangular ribbons. The desire to produce non-circular carbon fibres is driven by the readiness for stabilisation of such fibres (compared with round fibres with equivalent cross-sectional area) because non-circular fibres can have shorter oxygen diffusion distance from the surface. In addition, they tend to have better mechanical properties. However, cross-sectional areas of these fibres are still relatively small and the subject has been hindered by an insufficient understanding of microstructural control and numerous technical problems [Edie et al, Carbon, 1994, 32, 1045; Edie

-10-

et al, Carbon, 1993, 31, 941; Robinson et al, Carbon, 1996, 34, 13; Edie et al, High Temperatures-High Pressures, 1990, 22, 289; Mochida et al, J. Mater. Sci., 1993, 28, 2331; and Stoner et al, High Temperatures-High Pressures, 1990, 22, 299].

Ribbon fibres (Figure 3) can be beneficial for making a two-dimensional arrangement and are suitable for thermal management applications due to their linear structure which has high thermal conductivity compared with circular fibres. However known ribbon fibres have small transverse areas and the layer structures which allow graphite growth are constrained. Ribbon fibres developed by Edie et al and Mochida et al (supra) have small cross-sectional areas. Although different transverse textures are known for circular mesophase pitch-based carbon fibres (radial, onion-skin, flat-layer, radial-folded and random - see Figure 2), only line-origin texture has been reported for ribbon fibres. Edie et al used slot dies to produce ribbon fibres. The largest aspect ratio adopted was 9.

The present invention is based on the recognition that when the aspect ratio of the die slot is increased above conventional levels, the molecular orientation in the extruded and drawn tape undergoes a transition.

Thus viewed from one aspect the present invention provides a method for preparing mesophase pitch-based tapes comprising: extruding mesophase pitch through a die with an aspect ratio of 10 or more and drawing at a draw ratio greater than 5.

Preferably the mesophase tape is stabilised in a stabilisation step (eg oxidatively stabilised). Particularly preferably, stabilisation is followed by pressing to produce

-11-

bulk carbon material. The process may thereafter advantageously comprise the step of carbonisation.

Preferably the aspect ratio of the die is 20 or more, particularly preferably 30 or more, more preferably 40 or more, more especially preferably about 50.

As the aspect ratio is increased to 50, the degree of orientation of the molecules parallel to the plane of the tape increases. By carefully controlling the shear rate and extension rate, mesophase pitch-based tape may be produced in which the planar molecules arrange parallel to the tape surface instead of vertical to the surface. A die with an aspect ratio of 50 has been used to produce highly oriented continuous carbon tapes which have novel flat-layer transverse texture and a cross-sectional area about 100 times greater than conventional mesophase pitch-based carbon fibres. In addition, the tape maintains excellent mechanical properties. The tensile strength of the carbon tape with a cross-sectional area of $500 \times 10 (\mu\text{m})^2$ is of the order of 1GPa. This transverse area is equivalent to that of a circular fibre with a diameter of 80 μm . Such a circular fibres would take a few days to stabilise and once carbonised would only have a tensile strength of the order of 0.2GPa due to the presence of defects. The electrical resistivity of 2700°C heat-treated carbon tape with cross-sectional area $\sim 8000 (\mu\text{m})^2$ is $\sim 1.2 \mu\Omega\text{m}$. This is equivalent to that of the most thermally conductive known mesophase pitch-based carbon fibres K1100 which have been heat treated to 3000°C. This suggests that the novel carbon tapes may have lower electrical resistivity if they are heat-treated to 3000°C. The measured electrical resistivity indicates that high thermal conductivity is expected in accordance with Lavin et al, Carbon, 1993, 31, 1001 (see Figure 4).

-12-

In a preferred embodiment of the process of the invention, the carbon tape is subjected to an elevated temperature (eg 3000°C).

Viewed from a further aspect the present invention provides a mesophase pitch-based tape comprising a flat layer transverse texture.

Viewed from a yet further aspect the present invention provides a mesophase pitch-based tape comprising graphite basal planes parallel to the main surface of the tape.

Viewed from a yet still further aspect the present invention provides a mesophase pitch-based tape obtainable by extruding and drawing mesophase pitch through a die with an aspect ratio of 10 or more, preferably 20 or more, particularly preferably 30 or more, more preferably 40 or more, more especially preferably about 50. The draw ratio should be greater than 5, preferably greater than 10.

Due to the novel transverse texture of the tape, the shrinkage of the tape matches the shrinkage of the bulk material during heat treatment which prevents bulk material from cracking. The method of the invention produces high-density bulk carbon materials without any need for liquid phase impregnation or vapour phase infiltration.

The tape of the invention has novel orientation with graphite basal planes parallel to the main surface of the tape. This is beneficial to the development of extended graphitic plane structure. The tape may have two-dimensional graphitic properties due to the extended layer structure. The larger cross-sectional area advantageously provides smoother spinning and higher conversion rate thus reducing production costs. The invention represents an efficient method for

-13-

producing carbon materials for thermal management applications and has enormous commercial value.

In a preferred embodiment, the tape of the invention has an extended graphitic plane structure.

Viewed from a further aspect the present invention provides a bulk carbon material obtainable by processing a tape according to the invention as herein defined.

Highly oriented mesophase-based graphite (HOMG) materials from mesophase pitch tapes have properties which are superior to ThermalGraph® due to the two-dimensional extensive graphitic plane structure of the tapes and higher density of the final bulk product. Due to the high degree of orientation of the tape, the bulk graphite material is expected to have excellent transport properties.

In a preferred embodiment, the bulk carbon graphite material is obtainable by laminating or pressing the tapes. Pressing is preferred and may be conducted at a carefully chosen pressures for a suitable length of time. By controlling the pressures used during formation of the bulk carbon materials, it is possible to produce a family of bulk carbon materials with different thermal and mechanical properties. Preferably, the tapes should be stabilised prior to pressing.

Typically pressing may be carried out a pressure of about 5-10 tonnes at an elevated temperature (eg about 400°C) for an extended period of time (eg about 2 hours).

The method of the invention permits preparation of wider tapes or sheets having two-dimensional properties over a wider area. It may be possible to replace conventional two-dimensional woven fibre structures with tapes or sheets of

-14-

the invention in the manufacture of polymer matrix composites.

In a preferred embodiment, the tape or sheet is wound to make pipes or bars.

In a preferred embodiment, the tape is laminated with one or ~~more ceramic materials as interlayers to give oxidation resistance at high temperatures.~~

In a preferred embodiment, the tape or sheet is formed into a honeycomb structure.

In a preferred embodiment, the tape or sheet is laminated with fibres or ribbons to control the expansion coefficient.

In a preferred embodiment, the tape is mixed with stabilised tapes from oxidation resistant material [see for example: Lu et al, *Journal of Mater Sci*, 34, 571-578, 1999] to produce oxidation resistant bulk carbon material.

The bulk carbon materials of the invention can be utilised in the aerospace, nuclear, metallurgical, chemical, mechanical, electronic and electrical industry. In particular, they are best suited in areas where heat generation limits efficiency or leads to component failure such as in high power electronic devices, high energy friction and braking systems, propulsion and energy generation equipment, as well as processing equipment operating in corrosive environments. The low production costs of the method of the invention will assist widespread applications in these thermal management areas. Manufacturers will benefit from cheaper production cost and high performance products and user will benefit from improved devices with greater thermal properties and reliability.

-15-

The invention has been and will now be described in a non-limitative sense with reference to the Example and the accompanying Figures in which:

Figure 1: Schematic illustration of mesophase spheres coalescing to a larger sphere;

Figure 2: Schematic illustration of the transverse textures of circular carbon fibres;

Figure 3: Schematic illustration of the texture of a typical ribbon carbon fibre;

Figure 4: Relationship between electrical resistivity and thermal conductivity (Lavin et al, Carbon, 1993, 31, 1001);

Figure 5: Texture of typical carbon tape; and

Figure 6: Schematic illustrations of bulk carbon material from tapes and circular fibres.

Example

Mesophase pitch was melt extruded from a rectangular die with an aspect ratio of 50 and continuously wound on to carbon felt which was fastened on a roller. The as-spun tapes were oxidatively stabilised and then cut into desired length. The tapes were loaded into a rectangular mould along one direction and compacted under hot press with a ram pressure of 5-10 ton at a temperature of 400°C for 2 hours (see Fig. 6). These tapes soften under the effect of pressure and temperature and fuse together. However, the preferred orientation induced during extrusion and winding is retained. The bulk material was removed from the mould and heat treated under inert atmosphere to convert it into bulk carbon material.

For comparison, a circular fibre was used to make a similar bulk material. A schematic diagram of the various materials is shown in Figure 6. After carbonisation, the bulk carbon

-16-

material from circular fibres cracked into a few pieces. However the bulk carbon material from a tape of the invention maintained integrity with no obvious cracks developed on the surfaces. This is attributable to the circular fibre structural constraints which inhibit shrinkage while the parallel nature of the layer planes in the tapes allows shrinkage and dissipation of such stresses.

The advantage of pressing stabilised tapes into desired shape is that the size of bulk materials is not limited by the subsequent stabilisation process as in Amoco's method. Additionally the tapes may be pressed at higher pressure to achieve higher bulk density of the order of 1.8 Mgm^{-3} . For example, after carbonisation at 1000°C , the bulk carbon material has an apparent density of the order of 1.9 Mgm^{-3} and the tapes are closely bonded together with little inter-tape porosity. The bulk carbon material has preferred orientation of layer structure parallel to the main bulk carbon surface. The pressure used for formation of the bulk materials must be carefully controlled so as not to destroy the individual tape to ensure high strength of the bulk material. The bulk carbon materials obtained from tapes have higher density than those from circular fibres due to the lower porosity. This leads to a self-reinforced carbon material with two-dimensional ultra-high thermal conductivity at considerably reduced production cost.

1/6

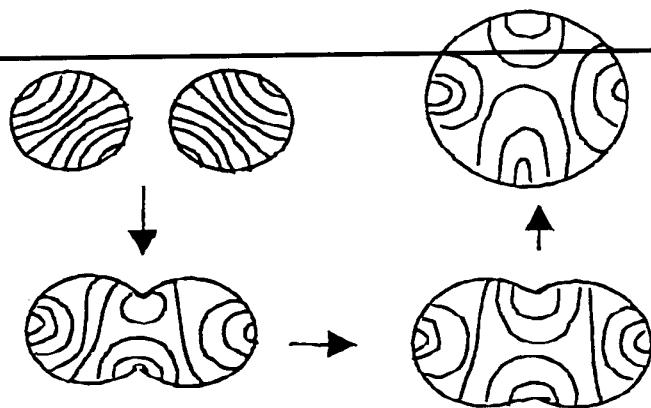
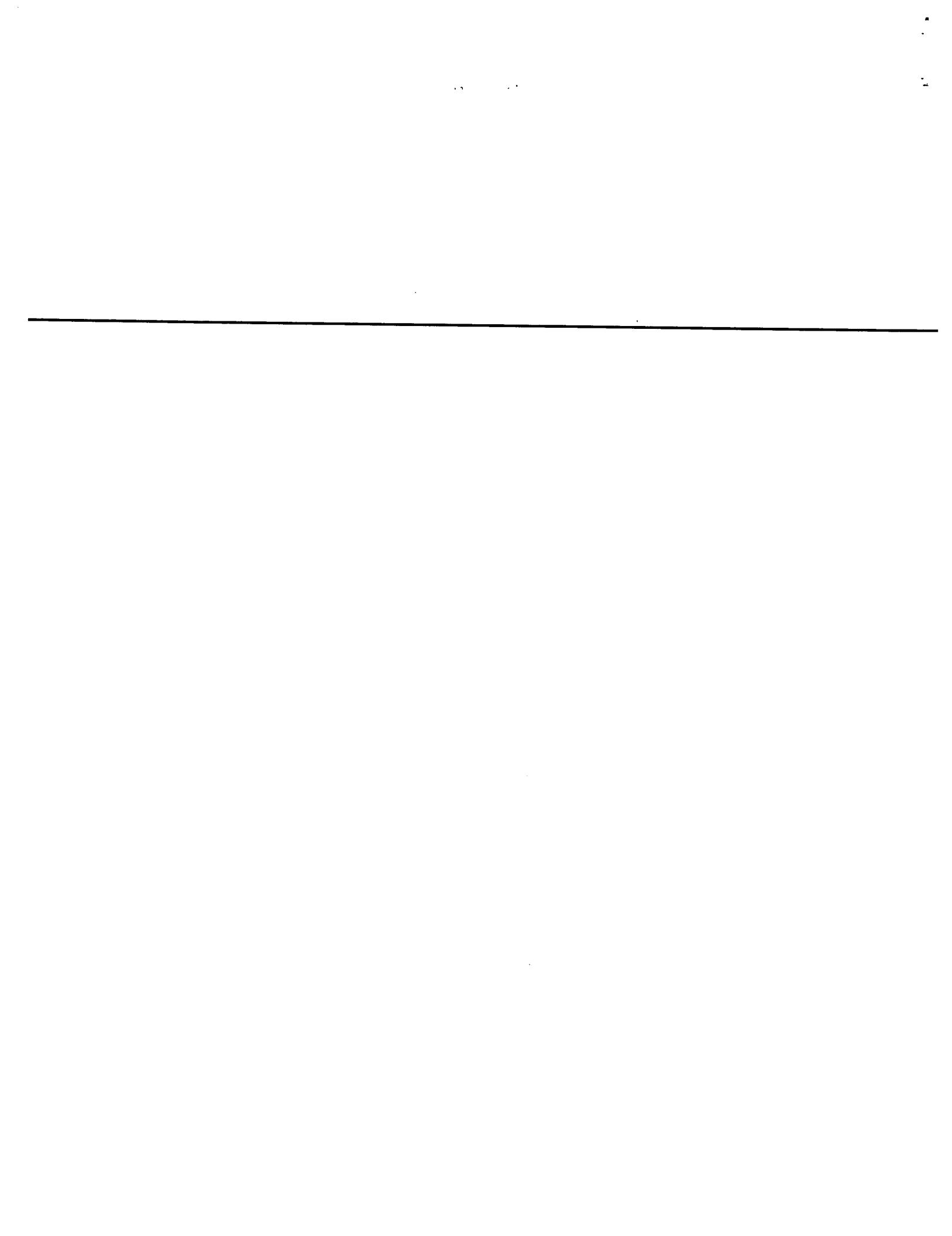
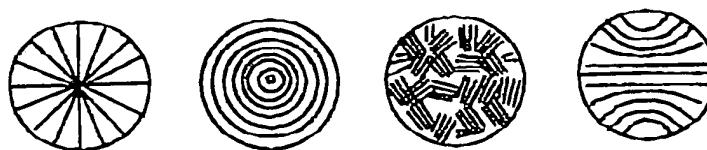


Fig. 1. The schematic diagram of mesophase spheres, coalescing to larger sphere

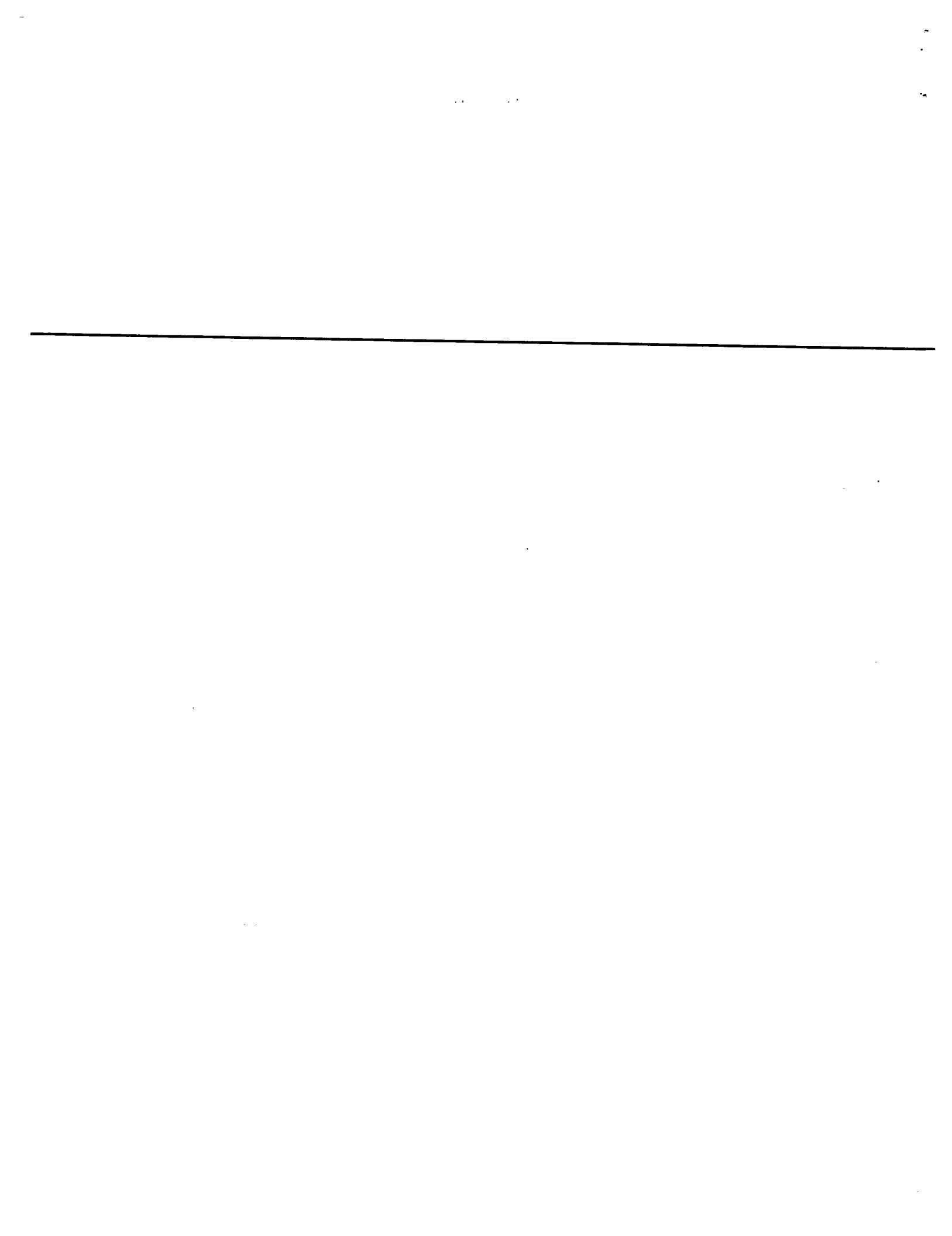


2/6



(a) Radial (b) Onion-skin (c) Random (d) Flat-layer

Fig. 2. Schematic drawing of the transverse textures found in circular carbon fibres



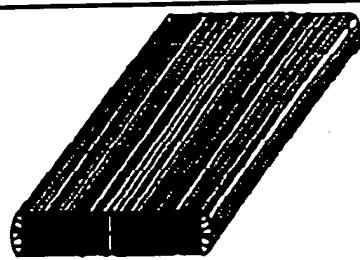
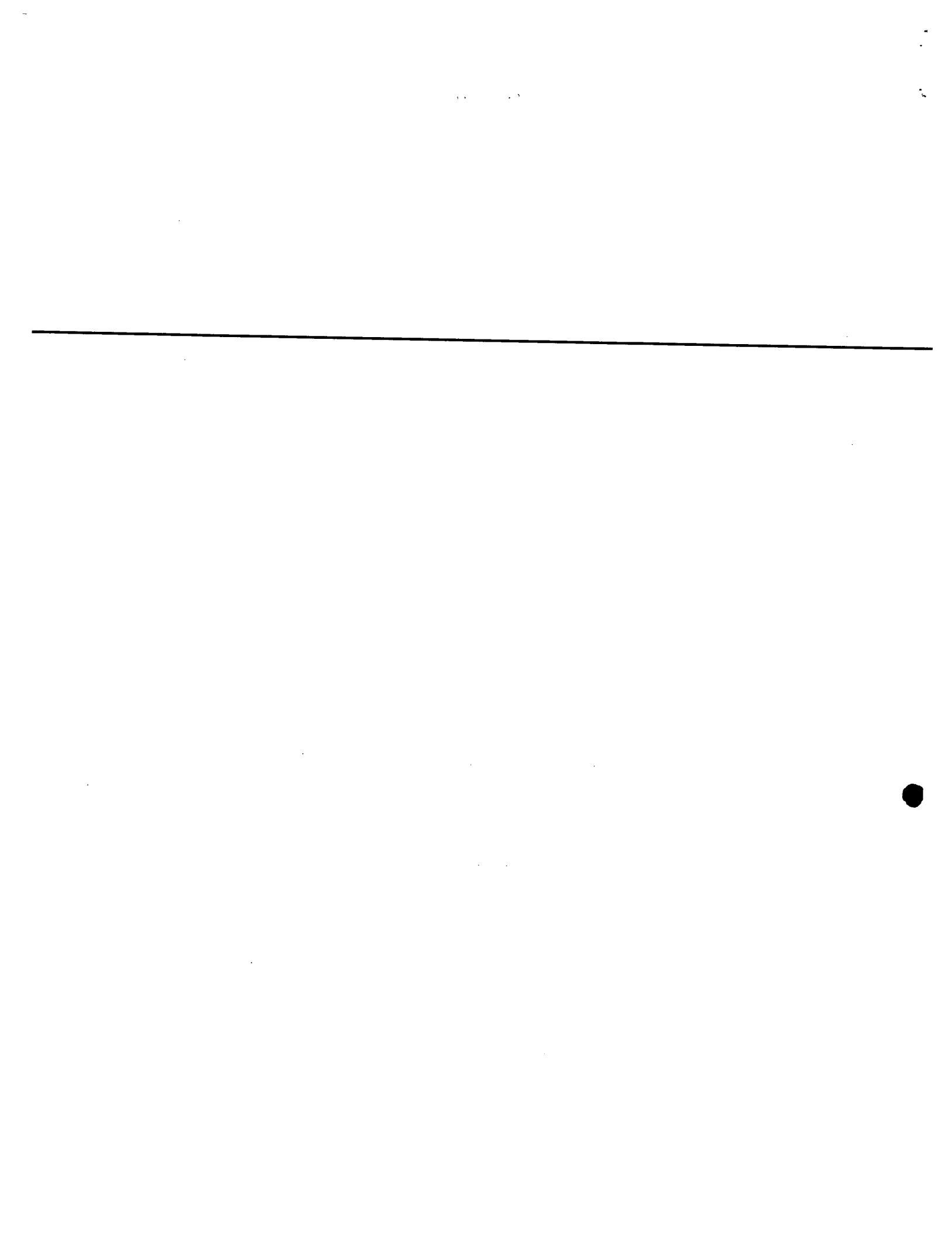


Fig. 3. Typical texture of ribbon carbon fibres



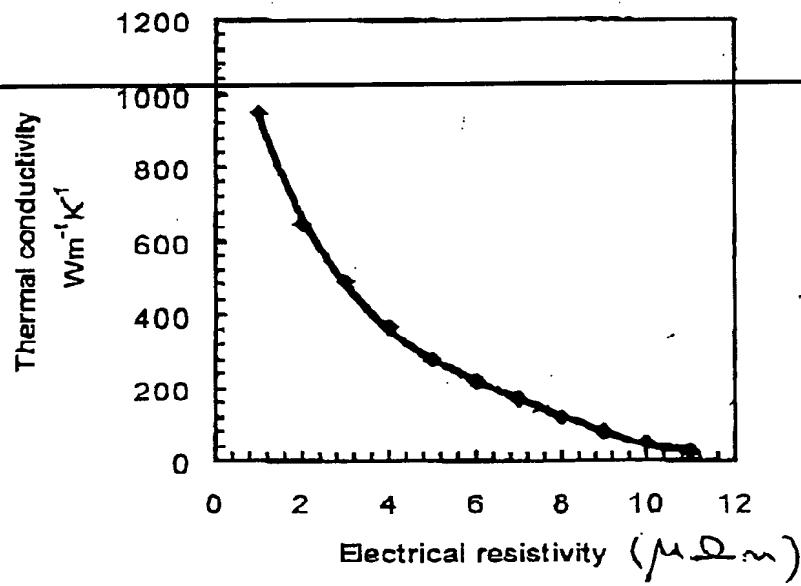
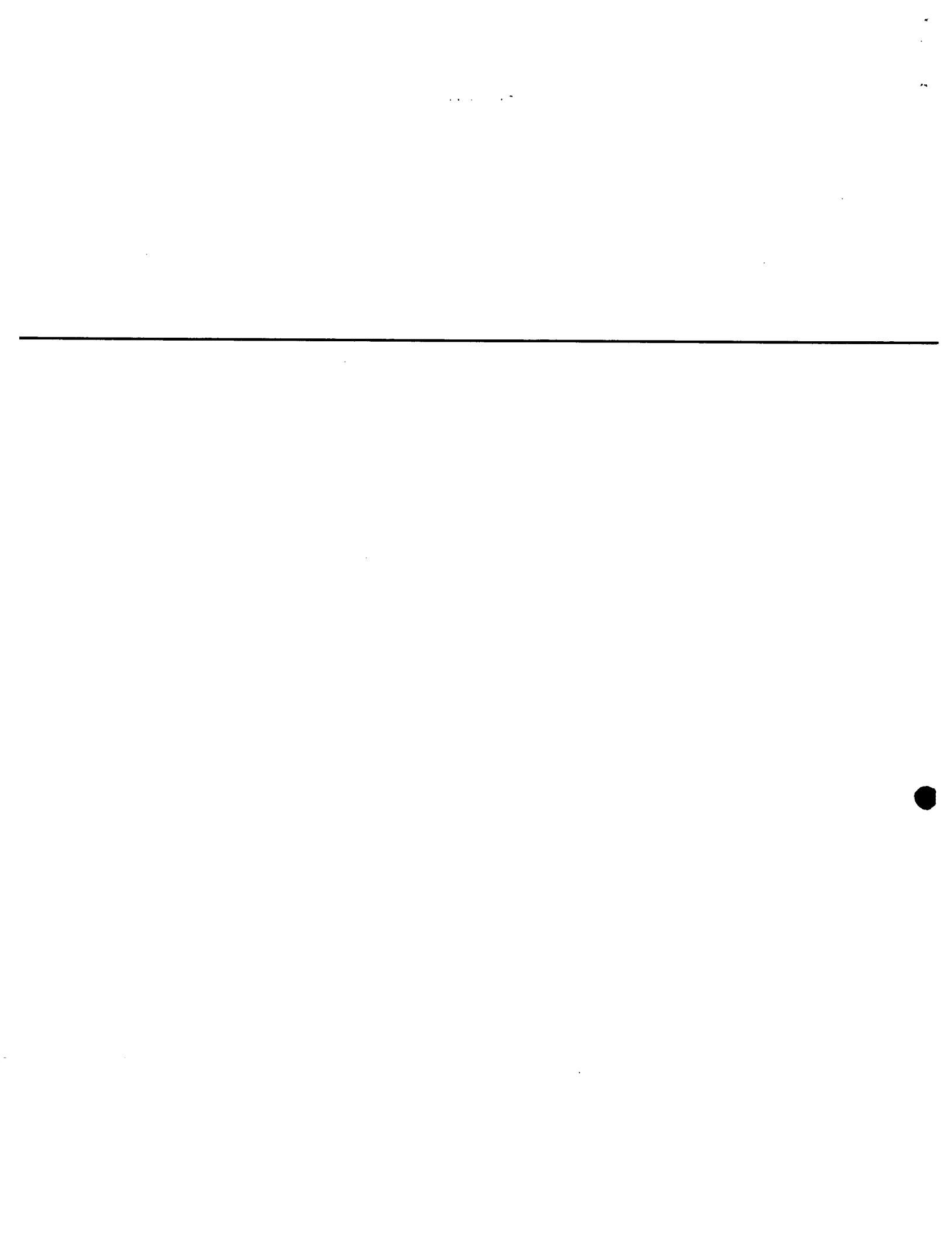


Fig. 4. Relationship between electrical resistivity and thermal conductivity
($\mu\text{ohm.m}$)



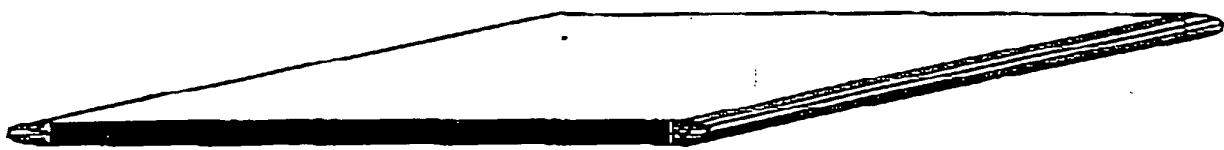
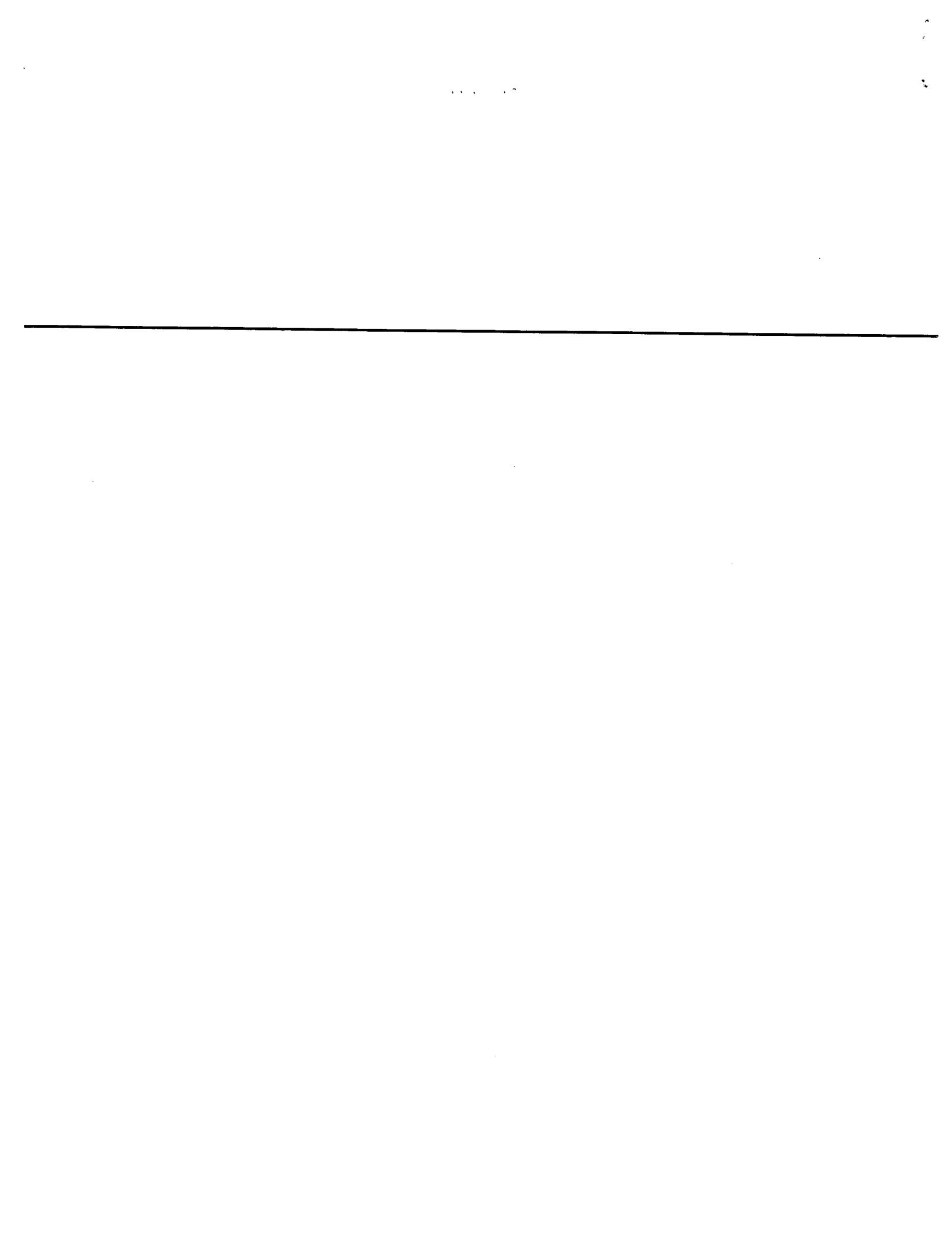


Fig. 5. Typical texture of carbon tape



6/6

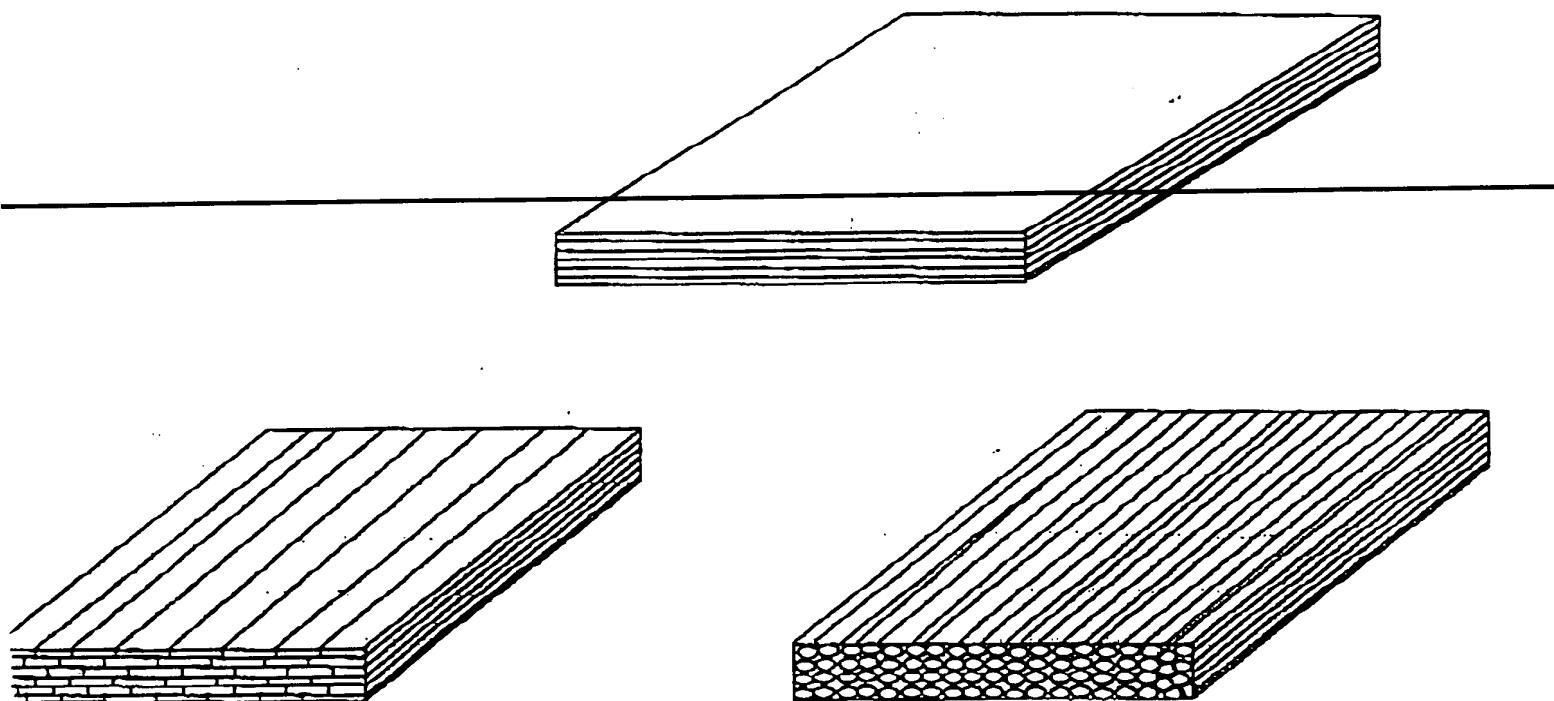


Fig. 6. Schematic diagram of bulk carbon material from tapes and circular fibres

PCT/GB00/02363

Urquhart Dykes & Lord

3 July 2000